



Recent Developments in the Photo Catalytic Applications of Polymer Nanocomposites - An Overview

M. Mubarak Ali*, D. John Williams

Department of Chemistry, Chikkaiah Naicker College, Erode, TN, India

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Abstract

Water pollution by synthetic dyes and heavy chemical substances has become the major issue around the globe after the rapid growth of industries and human activities. The dyes present in the contaminated water are non-biodegradable; hence it seriously affects human beings and the environment. A number of conventional techniques were investigated by researchers, such as chemical treatment, adsorption, biological treatment, and membrane-based separation to remove the pollutants from the water. Nevertheless, these techniques were not effective because this technique leaves some of the soluble organic compounds and bacteria, which are very hard to remove. Hence the researchers around the globe have put their effort to develop a stable approach to address the day to day deterioration of water. Despite all the above techniques the photocatalysis from the advanced oxidation process has emerged as an eco-friendly, convenient and simple technique for the degradation of pollutants by using sunlight (Visible) and ultraviolet light (UV). Recently polymer nanocomposites based photocatalyst was attracted for the treatment of wastewater due to its unique properties such as surface mobility, large surface area and superior magnetic and optical properties. Substantial work has been accomplished and reported on the superior photocatalytic activity of polymer nanocomposite. Hence this review is dedicated to highlighting the photocatalytic activity of polymer nanocomposites in the past decades and also the recent developments in the ultraviolet and visible light-responsive polymer nanocomposites for their potential applications in environmental remediation to maintain the quality of drinking water.

Keywords: Nanocomposites; Photo Catalyst; Polymer; Pollutants.

1. INTRODUCTION

Water is a precious natural resource for the existence of all living things. The objective of the United Nations is to have clean and quality water for all humans in the 21st century, but the industries such as textiles, leather and pharmaceutical industries, etc., discharge toxic wastes into the water resources. The wastewater from the different industries threatens human life directly and pollutes the environment (Mills and Lunte, 1997; Hager and Bauer, 1999). So some suitable techniques should be used to remove the contaminants from the water. Recently photocatalytic method was investigated and found as an inexpensive, green and effective technology for the degradation of pollutants by employing UV and natural sunlight, which is available for infinite years. The basic need for the treatment of water is to find a suitable material that should have unique properties with high separation capacity, low cost, porosity, and reusability. In the broad field of material science, nanotechnology provides suitable material for the treatment of water.

Research in the field of polymer nanocomposites based photocatalyst has gained wide attention to address the problem associated with water pollution due to its extraordinary optical properties towards photocatalytic activity. The metal oxide (semiconductors) alone cannot be used for photocatalytic applications due to the limited solar absorption (3-5%). In order to enhance the photocatalytic activity, the large bandgap semiconductor (metal oxide) was combined with a small bandgap polymer. The synergic effect between the polymers and metal oxide were exhibiting excellent photocatalytic activity under both ultraviolet light and natural sunlight irradiation. Hence the polymer nanocomposites based photocatalyst materials were considered promising materials for the photo-decomposition of the contaminants.

Recently, the polymer nanocomposites were synthesized precisely with enhanced photocatalytic responses in the UV and visible region. A number of polymer nanocomposites based photocatalyst has been fascinated greatly due to its potential in removing highly toxic and non-biodegradable compounds. The detailed review of literature about the polymer nanocomposites

***M. Mubarak Ali**

Email: mubarakscience@gmail.com

and their applications, particularly their photocatalytic activity, is not explored so far up to the knowledge of the authors. Hence this review is devoted to the recent advancements in the design, modification and applications of various polymer nanocomposites towards the degradation of toxic pollutants in water resources using the photocatalytic technique.

Mechanism of the photocatalytic reactions

When the incident light from the light source is equal or higher than the bandgap of the metal oxide (semiconductor), the electrons receive energy from the light photons and excited to the conduction band from the valence band, while the free holes remained in the valence band (VB). The photo-generated charge carriers (electrons and holes) then recombine in a very short period, and the energy will be released in the form of photons. When the holes and electrons possess higher energy, they will migrate to the catalyst surface to undergo reduction reactions with the electron acceptors adsorbed by the surface. While the holes react with hydroxyl groups present in the surface and form hydroxyl radicals. Hydroxyl radicals are the strongest oxidizing agent enhancing the degradation rate. However, the oxidation of the pollutants and the reduction of oxygen do not occur simultaneously. There will be an accumulation of electrons in the conduction band (CB), which will increase the rate of recombination of electrons and holes. Hence the prevention of electron accumulation is necessary for efficient photocatalytic oxidation. These redox reactions influence the fundamental photocatalytic mechanism.

Synthesis of various polymer nanocomposites for Photocatalytic applications

The present study highlights the synthesis of various polymer nanocomposites based photocatalyst by different synthetic routes for the removal of various organic dyes and inorganic compounds. Polymer

nanocomposites and their various method of synthesis were listed in Table.1.

Factors affecting the Photocatalytic activity of various Polymer nanocomposites

Effect of P^H on the Photocatalytic behaviour of various Polymer nanocomposites

The effect of P^H is one of the important parameter determining the adsorption efficiency. The adsorption process is influenced by the zero points of charge (zpc) of the adsorbent as well as the acidic strength (pKa) value of the dye, more precisely on the electrostatic interaction between the adsorbent and the pollutant. Hence the effect of P^H was evaluated by using the Graphene oxide (GO) / Polyaniline (PANI) composite at 30°C by keeping the concentration and amount of the composite constant. The pKa value of (Indigo Carmine) IC was determined from the P^H dependence of electronic absorption spectra. The P^H of the solution showed variation (5.5-11). Hence the phosphate buffer of 0.067M and the NaOH was added to increase the P^H value. The result obtained revealed that the change in the P^H of the dye solution has a negligible effect on the λ max of IC. At this pH range, no significant change was observed for the dye molecules, and this indicates that there is a relation between the pH and the removal percentage of IC. From the study, it was concluded that the adsorption of IC was higher at lower pH and showed a sharp decrease in the strong alkaline medium. When the pH was 12, the degradation efficiency was decreased for GO/PANI composite, and the reason may be the intramolecular hydrogen bonding between the carbon, oxygen atoms and N-H bonds within the molecules. The hydrogen bonds result in the weakness of the N-H bond of the PANI, consequently weaken the intermolecular interactions. Hence it results in the decrease of the degradation efficiency (Ali H. Gemeay et al. 2017).

Table.1. Various methods of synthesis of polymer nanocomposites and their applications in the removal of dyes

S.No	Name of the photocatalyst	Synthesis method	Name of the dye	Removal (%)	Reference
1	PANI/NiFe ₂ O ₄	Self-assembly	MB	88.1	ManoharR. Patil & Shrivastava, 2014
2	PANI/TiO ₂	Template free method	RB	96.0	Nur Aziera Jumat et al. 2017
3	MIP _{RHB} -PPy/TiO ₂	Molecular imprinting	RhB	85.0	He et al. 2014
4	PANI/TiO ₂	In-situ polymerization	MO	92.9	Ali Olad et al. 2012
5	PANI/ZnO	In-situ chemical polymerization	MB	90.0	Runjua Qin et al. 2018
6	PANI-Al ZnO	In-situ oxidative	RB	98.0	Mitraa et al. 2017

Abbreviation

PANI/NiFe₂O₄- Polyaniline-Nickel ferrite, PANI/TiO₂- Polyaniline-Titanium oxide, MIP_{RHB}-PPy/TiO₂- Molecular imprinted Rhodamine B Polypyrrole/Titanium Dioxide, MB- Methylene Blue, RhB-Rhoda mine-B, MO-Methyl Orange, RB-Reactive Black.

PMMA/ZnO nanocomposite was investigated (Alessandro Di Mauro et al. 2017) for the photocatalytic activity and reported that the P^H of the solution greatly influenced the photocatalytic activity. Since the wastewater from the industries presents either acidic or basic in nature, so the P^H of the solution should be considered during the photocatalytic activity. So by using different P^H of the MB solutions, the experiments were carried out and reported that the photocatalytic activity was zero at $P^H=3$ because of the dissolution of ZnO at low P^H . When the P^H of the solution was increased to 12, there is an excess of hydroxyl ions which accelerates the photocatalytic activity. Photocatalytic activity of polymer nanocomposites for various dyes at different P^H under UV and visible light irradiation were listed in Table.2

Effect of irradiation time on the Photocatalytic activity of various Polymer nanocomposites

Recent studies on the photocatalytic activity of the Polyaniline/Zinc oxide (PANI/ZnO) composite was investigated by vanja gilja et al. 2018 under visible light irradiation by employing the organic dye (acid blue) model wastewater. From the study, it was concluded

that the composite removed almost 90% of the dye in 60 min. The first-order rate constants revealed that the morphology and surface of the photocatalyst remarkably influenced the photocatalytic activity.

Shengying Li et al. (Shengying Li et al. 2009) fabricated PPy/TiO₂ nanocomposites and evaluated the photocatalytic activity of the nanocomposites. When the polymer (PPy) was used, the degradation efficiency was 50.25% under the same conditions. At the same time, PPy/TiO₂ nanocomposites were used its degradation efficiency was 40.35 for 10min and 75.42% after 30 min under visible light irradiation. The reason for the degradation efficiency of the PPy/TiO₂ nanocomposite is that the methyl orange is an azo dye with an aryl ring as the main chromophore. The decolouration of the methyl orange is the result of the rupture of the conjugative system (conjugative system made up of azo group) and unable to destroy the N-N bond completely. After 120 min, the degradation efficiency was increased to 95.54%. From the result, it can be understood that the PPy plays a major role in photocatalytic activity. It is further concluded that the TiO₂ in the PPy matrix improved the photocatalytic activity.

Table. 2. Photocatalytic activity of Polymer nanocomposites at various P^H levels.

S.No	Name of the photocatalyst	Initial dye conc.	P^H	Conc. of the catalyst	Name of the dye	Removal %	Reference
1	PANI/TiO ₂	50mg/L	3	1g/L	Rb-19	100.0	Shankamma Kalikeri et al. 2018
2	PANI/TiO ₂ /GO	25ppm	7	800mg/L	RB	90.0	Azad Kumar et al. 2018
3	PANI/TiO ₂ /GN	10.5mg/L	9	50mg	MB	87.0	Rajeev Kumar et al. 2016
4	15PANI/TiO ₂	30mg/L	3	1g/L	RR45	79.7	Vanja Gilja et al. 2017
5	Bi ₂ O ₂ CO ₃ /PPy/g-C ₃ N ₄	0.5mM	7	50mg	RhB	98.9	Wei Zhao et al. 2017

Abbreviation

PANI/TiO₂- Polyaniline-Titanium oxide PANI/TiO₂/GO- Polyaniline-Titanium Dioxide Graphene Oxide, PANI/TiO₂/GN- Polyaniline/Titanium Dioxide/Graphene nanosheets, Rb 19-Reactive Blue-19, RB-Reactive Black, MB-Methylene Blue, RR 45-Reactive Red 45.

Table. 3. Photocatalytic activity of polymer nanocomposites at different irradiation time

S.No	Name of the photocatalyst	Initial dye conc.	Name of the dye	Conc. of the catalyst	Irradiation time	Removal %	Reference
1	PPy/1-D ZnO	5ppm	CV	1g/L	120 min	97.1	Pritam Patil et al. 2016
2	PANI/HD ZnO	3×10^{-5}	MO	40mg	120min	94.0	Pei et al. 2014
3	PVA/TiO ₂ /G-MwCNT	50ml	MB	10mg/L	24 hrs	90.0	Gown Jung and Hyung-II Kim, 2014
4	PPy/Fe ₃ O ₄ /ZnO	200ml	MO	0.2g	4 hrs	85.2	Liang An et al. 2014
5	PANI/ZnO	1.3×10^4	MB	50mg/L	5 hrs	97.0	Eskizeybek et al. 2012

Abbreviation

PPy/1-D ZnO- Polypyrrole/1-Dimensional Zinc Oxide, PANI/HD ZnO- Polyaniline/Hybrid defective Zinc Oxide, PVA/TiO₂/G-MwCNT- Polyvinyl alcohol/Titanium Dioxide/Graphene-Multiwall carbon nanotubes, PPy/Fe₃O₄/ZnO- Polypyrrole/Iron Oxide/Zinc Oxide, MO-Methyl Orange, MB-Methylene Blue, CV-Crystal Violet.

Ternary ZnO/reduced graphene oxide (rGO)/polyaniline (PANI) nanocomposite has been studied (Huipeng Wu et al. 2016) for the photocatalytic activity against methyl orange (MO) and reported that the degradation efficiency was reached almost 100% within 1 hour under UV light irradiation. Photocatalytic activity of polymer nanocomposites for various dyes at different irradiation time under UV and visible light were listed in Table.3

Effect of concentration of the dye on the Photocatalytic activity of various Polymer nanocomposites

Recent studies on the initial concentration of the dye (Methylene Blue) on the photocatalytic activity of the PPy/TiO₂ (Murugan Sangarswari and Mariappan Meenakshi Sundaram, 2017) nanocomposite and TiO₂ was evaluated under the visible light (sunlight) irradiation within the concentration range of 10-60 ppm with the catalyst amount and irradiation time kept constant. The result concluded that the PPy/TiO₂ nanocomposite exhibited a high efficiency than the TiO₂. When the concentration of the dye was increased from 10 to 20 ppm, the degradation efficiency of MB was decreased to 90 (5%). Further, the concentration was increased to 60 ppm the degradation efficiency was decreased to 25%. The reason for the decrease of the degradation efficiency may be the dye with a higher concentration may act as an inner filter that moves the photons from the catalyst surface and the non-availability of oxidative free radicals. Further, the inverse effect, (i.e.) when the concentration of the dye increases, it adsorbed on the catalyst surface active site. When the dye concentration increased, there will be no space for the formation of OH* radicals (hydroxyl radicals is the strongest oxidizing agent enhancing the degradation rate). Hence it leads to degradation efficiency.

Fei Gao et al (2016) fabricated PPy/TiO₂ nanocomposites and TiO₂ and investigated the photocatalytic activity. The result indicates that the degradation efficiency of the fabricated PPy/TiO₂ was higher than the pure TiO₂. The study was evaluated by varying the molar ratio of PPy/TiO₂ from 1:20 to 1:100. When the composition of the TiO₂ was increased from 1:100 to 1:140, the nanocomposite showed a decrease in photocatalytic efficiency. The reason for the decreased activity may be the PPy layer encapsulated the TiO₂ to higher extent, which hinders the absorption of light. The PPy layer may also hinder the contact between photogenerated holes and OH⁻ and H₂O species and hinders the formation of OH* radicals. When the ratio of PPy/TiO₂ was 1:100 the degradation efficiency was 97% at 8 hrs which is more than 41% higher than that of pure TiO₂.

Recently Rajeev kumar et al fabricated three various nanocomposites Ag/TiO₂, TiO₂/PPy and Ag/TiO₂/PPy. The study on the effect of the initial dye concentration disclosed that the visible light degradation of MB was decreased from 100% to 83%, whereas the visible light was decreased from 100% to 18.85% in which the concentration was increased from 4 to 20 mg/L. From the result obtained, it was concluded that the Ag/TiO₂/PPy nanocomposites were effective among the three nanocomposites, which can be used for the photodegradation of organic pollutant (Rajeev Kumar et al. 2016). An effective and low-cost TiO₂/Polystyrene Floating photocatalyst was synthesized by Singh, S et al and studied the effect of photocatalyst amount for the photocatalytic activity and reported that the maximum degradation efficiency of 93% was achieved when the photocatalyst amount was around 10 wt%. This study promises that this photocatalyst can further be used for commercial applications (Singh et al. 2015). Photocatalytic activity of polymer nanocomposites for various dyes at a different concentration under UV and visible light irradiation were listed in Table.4

Table. 4. Photocatalytic activity of polymer nanocomposites at various concentration of the dye

S. No	Name of the photocatalyst	Catalyst conc.	Dye	Initial dye conc.	Removal %	Reference
1	PANI/MoO ₃	500mg	MB	1.5×10 ⁻⁵ mol/L	95.4	Dhanavel et al. 2017
2	PANI/Cu ₂ O	50mg	MO	10 ⁻⁵ M	99.0	Xiufang Wang et al. 2013
3	PANI/CuI/rGO	50mg	RhB	1.0×10 ⁻⁵ mol/L	96.0	Xiufang Wang et al. 2016
4	PANI-N-HTiNbO ₅	30mg	MB	1×10 ⁻⁵ M	97.8	Chao Liu et al. 2014
5	PANI/M-Cu ₂ O	0.8g/L	TP	600ppm	100.0	Mohamed and Aazam, 2014
6	PANI/SWCNT	2wt%	RB	1×10 ⁻⁵ M	95.9	Mukulika Jana Chatterjee et al. 2017
7	PAZ/ZnO	500mg	MB	500ppm	97.0	Pradeeba and Sampath, 2018

Abbreviation

PANI/MoO₃- Polyaniline/Molybdenum Trioxide, PANI/Cu₂O- Polyaniline/Copper Oxide, PANI/CuI/rGO- Poly aniline/copper Iodide/reduced Graphene Oxide, PANI-N-HTiNbO₅- Polyaniline-Nitrogen-doped Titanoniobic acid, MB-Methylene Blue, MO-Methyl Orange, RhB-Rhoda mine-B, TP-Thiophene, PAZ/ZnO -Poly(azomethine)/Zinc oxide

Comparative study on the Photocatalytic activity of various polymer nanocomposites under ultraviolet (UV) and visible light (sunlight)

S.No	Name of the photocatalyst	Catalyst conc.	Dye	Initial dye conc.	Removal %		Reference
					UV	Sunlight	
1	PANI/ZnO	0.4mg/ml	MB	1×10^{-5} M	79	97	Volkan Eskizeybek et al. 2012
2	PANI/ZnO	0.4mg/ml	MG	1×10^{-5} M	89	99	
3	PANI/CdO	0.4mg/ml	MB	1.5×10^{-5} M	92	98	Handan Gulce et al. 2013
4	PANI/CdO	0.4mg/ml	MG	1.5×10^{-5} M	97	99	

Abbreviation

PANI/ZnO-Polyaniline/Zinc oxide, MB-Methylene Blue, MG- Malachite green

The photocatalytic activity of PEDOT/GO/MnO₂ ternary nanocomposites was investigated by Li Zhang et al. (2015) for the Methylene blue (MB) dye in both the visible and ultraviolet regions. It was found that the degradation efficiency of the nanocomposite under UV light was 97.1% and 98.9% under natural sunlight. The PEDOT/GO/MnO₂ nanocomposite exhibited a higher photocatalytic activity under natural sunlight than the UV light because the GO is a superior electron acceptor and transporter, which decreased the recombination of charge carriers and improved the photocatalytic activity. Moreover, the pure PEDOT absorbs the visible light and generates an electron (e⁻) which leads to the formation of oxyradicals, and charge separation takes place. The more amount of oxyradicals results in higher degradation under natural sunlight.

Recent studies on the degradation efficiency of the fabricated PEDOT/ZnO nanocomposite was investigated by Z. Katančić, et al. (2017) by using the RR45 dye in wastewater under both the simulated visible (sunlight) and UV irradiation. The PEDOT/ZnO (1:2) nanocomposite showed the highest degradation efficiency, and almost 37% of the dye was removed. The higher adsorption of the contaminant on the catalyst surface reduces the degradation efficiency. The photocatalytic activity under UV light irradiation was carried out for 90 minutes with an initial concentration of 30 mgL⁻¹. 25% of the dye was left in the wastewater. Whereas the PEDOT/ZnO with (1:3) and (1:5) showed very low degradation efficiency, and the dye left in the wastewater was 82% and 91%. The Photocatalytic activity under simulated sunlight was evaluated and reported that when the PEDOT/ZnO (1:2) nanocomposite was employed, around 53% of the dye was left in the wastewater after 90 minutes. Further, it was concluded that the nanocomposite degrades 10% of the dye every 15 minutes. The reason for the high degradation efficiency is the synergic effect between the PEDOT and ZnO. The PEDOT/ZnO with a higher concentration showed low degradation. The reason for the low degradation of PEDOT/ZnO is due to the congestion of the ZnO catalyst in the polymer.

CONCLUSION

In this review article, we have comprehensively reviewed the various synthetic methods, their unique properties and recent developments in the field of polymer nanocomposites for the effective removal of pollutants in water using the advanced photocatalytic technique. Polymer nanocomposites exhibit better photodegradation activity towards pollutants under light irradiation due to the large exposed area, effective migration and separation of charge carriers, as well as the high electrostatic interaction between the catalyst and the pollutants due to its outstanding properties. The research in the area of water treatment using polymer nanocomposites is appreciable, but still, there is enough room to explore in terms of the design and synthesis of materials. There is certainly visible light response polymer-metal oxide-based photocatalyst materials are significant. Hence to enhance the practicability of visible light response, the drawback of using polymer nanocomposite as photocatalyst should be focused on in the future. Care should be taken in order to design the polymer nanocomposite with favourable physicochemical properties and also the suspension of the pollution, which may be an obstacle for photocatalytic performances.

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REFERENCES

- Alessandro Di Mauro, Maria Cantarella, Giuseppe Nicotra, Giovanna Pellegrino, Antonino Gulino, Maria Violetta Brundo, Vittorio Privitera and Giuliana Impellizzeri, Novel synthesis of ZnO/PMMA nanocomposites for photocatalytic applications, *Scientific Reports*, 7, 01-12(2017).
doi:10.1038/srep40895

- Ali H. Gemeay, · Rehab G. El-Sharkawy and · Eman F. Aboelfetoh, Graphene oxide/polyaniline/manganese oxide ternary nanocomposites, facile synthesis, characterization and application for indigo carmine removal, *J. Polym. Environ.*, 26(2), 655-669(2017).
doi: 10.1007/s10924-017-0947-z
- Ali Olad, Sepideh Behboudi and Ali Akbar Entezami, Preparation, characterization and photocatalytic activity of TiO₂/polyaniline core-shell nanocomposite, *Bull. Mater. Sci.*, 35(5), 801–809(2012).
- Azad Kumar, Gajanan Pandey, Comparative Photocatalytic Degradation of Rose Bengal Dye under Visible Light by TiO₂, TiO₂/PAni and TiO₂/PAni/GO Nanocomposites, *Ijrasnet*, 6(2) 339-350(2018).
doi:10.22214/ijrasnet.2018.2049
- Chao Liu, Liang Wu, Jing Chen, Ji-yuan Liang, Changshun Li, Hong-mei Ji, Wen-hua Hou, The nanocomposite of polyaniline and nitrogen-doped layered HTiNbO₅ with excellent visible-light photocatalytic performance, *Phys. Chem. Chem. Phys.*, 16, 13409-13417(2014).
doi:10.1039/C4CP01423E
- Dhanavel, S., Nivethaa, E. A. K., Narayanan, V. and Stephen, A., In vitro cytotoxicity study of dual drug-loaded citosan/palladium nanocomposite towards HT-29 cancer cells, *Mech. Mater. Sci. Eng.*, 75(1) 1399-1410(2017).
doi:10.1016/j.msec.2017.03.058
- Eskizeybek, V., Sari, F., Ice, H. G., Ice, A. G. and Avcı, A., Preparation of the new polyaniline/ZnO nanocomposite and its photocatalytic activity for degradation of methylene blue and malachite green dyes under UV and natural sun lights irradiations, *Appl. Catal. B: Environ.*, 119-120, 197–206(2012).
doi:10.1016/j.apcatb.2012.02.034
- Fei Gao, Xianhui Hou, Aolan Wang, Guangwen Chu, Wei Wu*, Jianfeng Chen, Haikui Zou, Preparation of polypyrrole/TiO₂ nanocomposites with enhanced photocatalytic performance, *Particuology*, 26, 73-78(2016).
doi:10.1016/j.partic.2015.07.003
- Gown Jung, Hyung-II Kim, Synthesis and photocatalytic performance of PVA/TiO₂/Graphene-MWCNT nanocomposites for dye removal, *J. Appl. Polym. Sci.*, 131(17), 1-7(2014).
doi:10.1002/app.40715
- Hager, S. and Bauer, R., Heterogeneous photocatalytic degradation of organics by UV-irradiated titanium dioxide for air purification, *Chemosphere*, 38(7), 1549–1559(1999).
doi: 10.1016/s0045-6535(98)00375-0
- Handan Gulce, Volkan Eskizeybek, Bircan Haspulat, Fahriye Sari Ahmet Glce, and Ahmet Avcı, Preparation of a New Polyaniline/CdO Nanocomposite and Investigation of Its Photocatalytic Activity: Comparative Study under UV Light and Natural Sunlight Irradiation, *Ind. Eng. Chem. Res.*, 52(32), 10924-10934(2013).
doi: 10.1021/ie401389e
- He, M. Q., Bao, Sun, K. Y., Zhao, D. X., Li, W. B., Xia, J. X. and Li, H. M., Synthesis of molecularly imprinted polypyrrole/titanium dioxide nano composites and its selective photocatalytic degradation of rhodamine B under visible light irradiation, *Express Polymer Letters*, 8(11), 850-861(2014).
doi: 10.3144/expresspolymlett.2014.86
- Huipeng Wu, Shengling Lin, Chuanxiang Chen, Wei Liang, Xiaoyan Liu and Hongxun Yang, A new ZnO/rGO/polyaniline ternary nanocomposite as photocatalyst with improved photocatalytic activity, *Mater. Res. Bull.*, 83, 434-441(2016).
doi:10.1016/j.materresbull.2016.06.036
- Katančić, Z., Šuka, S., Vrbat, K., Tašić, A. and Hrnjak-Murčić, Z., Synthesis of PEDOT/ZnO photocatalyst: Validation of photocatalytic activity by degradation of azo RR45 dye under solar and UV-A irradiation, *Chem. Biochem. Eng. Q.*, 31(4), 385–394(2017).
doi: 10.15255/CABEQ.2017.1124
- Li Zhang, Ruxangul Jamal, Qin Zhao, Minchao Wang and Tursun Abdiryim, Preparation of PEDOT/GO, PEDOT/MnO₂, and PEDOT/GO/MnO₂ nanocomposites and their application in catalytic degradation of methylene blue, *Nanoscale Research Letters*, 10, 148(2015).
doi:10.1186/s11671-015-0859-6
- Liang An, Guanghui Wang, Xiaoming Shi, Min Su, Fang Gao, and Yang Cheng, Recyclable Fe₃O₄/ZnO/PPy composite photocatalyst: Fabrication and photocatalytic activity, *Russ. J. Phys. Chem. A.*, 88(13), 2419–2423(2014).
doi:10.1134/s0036024414130093
- Manohar R. Patil, Shrivastava, V. S., Photocatalytic degradation of carcinogenic methylene blue dye by using polyaniline-nickel ferrite nano-composite, *Der Chemica Sinica*, 5(2), 8-17(2014).
- Mills, A. and Lunte, S., An overview of semiconductor photocatalysis, *J. Photochem. Photobiol.*, 108, 01–35(1997).
doi:10.1016/S1010-6030(97)00118-4
- Mitra, M., Ghosh, A., Mondal, A., Kargupta, K., Ganguly, S. and Banerjee, D., Facile synthesis of aluminium doped zinc oxide-polyaniline hybrids for photoluminescence and enhanced visible-light assisted photo-degradation of organic contaminants, *Appl. Surf. Sci.*, 402, 418–428(2017). DOI: 10.1016/j.apsusc.2017.01.072

- Mohamed, R. M. and Aazam, E. S., Preparation and characterization of core-shell polyaniline/mesoporous Cu₂O nanocomposites for the photocatalytic oxidation of thiophene, *Applied catalysis A: General*, 480, 100-107(2014).
[doi:10.1016/j.apcata.2014.04.039](https://doi.org/10.1016/j.apcata.2014.04.039)
- Mukulika Jana Chatterjee, Amrita Ghosh, Anup Mondal and Dipali Banerjee, Polyaniline–single-walled carbon nanotube composite – a photocatalyst to degrade rose bengal and methyl orange dyes under visible-light illumination, *RSC Adv.*, 7, 36403–36415(2017).
[doi: 10.1039/C7RA03855K](https://doi.org/10.1039/C7RA03855K)
- Murugan Sangaeswari, Mariappan Meenakshi Sundaram, Development of efficiency improved polymer-modified TiO₂ for the photocatalytic degradation of an organic dye from wastewater environment, *Appl. Water Sci.*, 7(4), 1781–1790(2017).
[doi:10.1007/s13201-015-0351-6](https://doi.org/10.1007/s13201-015-0351-6)
- Nur Aziera Jumat, Phang Sook Wai, Juan Joon Chng, Wan Jeffrey Basirun, Synthesis of polyaniline-TiO₂ nanocomposites and their application in photocatalytic degradation, *Polymers & Polymer Composites*, 25(7), 507-514(2017).
[doi:10.1177/096739111702500701](https://doi.org/10.1177/096739111702500701)
- Pei, Z., Ding, L., Lu, M., Fan, Z., Weng, S., Hu, J. and Liu, P., Synergistic effect in polyaniline-hybrid defective ZnO with enhanced photocatalytic activity and stability, *J. Phys. Chem. C*, 118(18), 9570–9577(2014).
[doi:10.1021/jp5020143](https://doi.org/10.1021/jp5020143)
- Pradeeba, S. J. and Sampath, K., A comparative study of photocatalytic degradation efficiency of methylene blue dye in wastewater using poly (Azomethine)/ZnO nanocomposite and poly (Azomethine)/TiO₂ nanocomposite, *Journal of Ovonic Research*, 14(3), 243 – 259(2018).
- Pritam Patil, Ganesh Gaikwad, D R Patil and Jitendra Naik, Synthesis of 1-D ZnO nanorods and polypyrrole/1-D ZnO nanocomposites for photocatalysis and gas sensor application, *Bull. Mater. Sci.*, 39(3), 655–665(2016).
[doi:10.1007/s12034-016-1208-9](https://doi.org/10.1007/s12034-016-1208-9)
- Rajeev Kumar, Mohammad Omaish Ansari, Nazish Parveen, Mohammad Oves, Barakat, M. A., Ahmed Alshahri, Mohd. Yusuf Khan and Moo Hwan Cho, Facile route to a conducting ternary polyaniline @ TiO₂/GN nanocomposite for environmentally benign applications: photocatalytic degradation of pollutants and biological activity, *RSC Adv.*, 6(112), 111308-111317(2016).
[doi:10.1039/C6RA24079H](https://doi.org/10.1039/C6RA24079H)
- Rajeev Kumar, Reda M. El-Shishtawy, and Mohamed A. Barakat, Synthesis and characterization of Ag-Ag₂O/TiO₂ @ polypyrrole heterojunction for enhanced photocatalytic degradation of methylene blue, *Catalysts*, 6(6), 76(2016).
[doi:10.3390/catal6060076](https://doi.org/10.3390/catal6060076)
- Runhua Qin, Lingyun Hao, Yi Liu, Yueling Zhang, Polyaniline-ZnO hybrid nanocomposites with enhanced photocatalytic and electrochemical performance, *Chemistry Select*, 3(23), 6286-6293(2018).
[doi:10.1002/slct.201800246](https://doi.org/10.1002/slct.201800246)
- Shankramma Kalikeri, Nidhi Kamath, Dhanashri Jayant Gadgil, and Vidya Shetty Kodialbail, Visible light-induced photocatalytic degradation of reactive blue-19 over highly efficient polyaniline-TiO₂ nanocomposite: a comparative study with solar and UV photocatalysis, *Environ. Sci. Pollut. Res.*, 25(4), 3731-3744(2018).
[doi:10.1007/s11356-017-0663-1](https://doi.org/10.1007/s11356-017-0663-1)
- Shengying Li, Mingkai Chen, Lijun He, Fei Xu, and Guohu Zhao, Preparation and characterization of polypyrrole/TiO₂ nanocomposite and its photocatalytic activity under visible light irradiation, *J. Mater. Res.*, 24(8), 8(2009).
[doi:10.1557/jmr.2009.0316](https://doi.org/10.1557/jmr.2009.0316)
- Singh, S., Singh, P. K. and Mahalingam, H., An effective and low-cost TiO₂/polystyrene floating photocatalyst for environmental remediation, *Int. J. Environ. Res.*, 9(2), 535-544(2015).
- Vanja Gilja, Ivan Vrbanić, Vilko Mandić, Mark Žić and Zlata Hrnjak-Murđić, Preparation of a PANI/ZnO composite for efficient photocatalytic degradation of acid blue, *Polymers*, 10(9), 940(2018).
[doi:10.3390/polym10090940](https://doi.org/10.3390/polym10090940)
- Vanja Gilja, Katarina Novaković, Jadranka Travaš-Sejdić, Zlata Hrnjak-Murđić, Marijana Kraljić, Roković and Mark Žić, Stability and Synergistic effect of polyaniline/TiO₂ photocatalysts in degradation of azo dye in wastewater, *Nanomaterials*, 7(12), 412(2017).
[doi:10.3390/nano7120412](https://doi.org/10.3390/nano7120412)
- Volkan Eskizeybek, Fahriye Sarı, Handan Gulce, Ahmet Gulce, Ahmet Avci, Preparation of the new polyaniline/ZnO nanocomposite and its photocatalytic activity for degradation of methylene blue and malachite green dyes under UV and natural sun lights irradiations, *Appl. Cat. B: Environ.*, 119–120, 197–206(2012).
[doi:10.1016/j.apcatb.2012.02.034](https://doi.org/10.1016/j.apcatb.2012.02.034)
- Wei Zhao, Yun Wang, Aijian Wang, Jun Qian, Weihua Zhu, Shengping Dou, Qian Wang, Qin Zhongc and Aihua Chen, Novel Bi₂O₂CO₃/polypyrrole/g-C₃N₄ nanocomposites with efficient photocatalytic and nonlinear optical properties, *RSC Adv.*, 7(13), 7658–7670(2017).
[doi:10.1039/C6RA28346B](https://doi.org/10.1039/C6RA28346B)

Xiufang Wang, Guangmei Chen, Jun Zhang, Synthesis and Characterization of novel Cu₂O/PANI composite photocatalysts with enhanced photocatalytic activity and stability, *Cat. Com.*, 31, 57-61(2013).
[doi:10.1016/j.catcom.2012.11.012](https://doi.org/10.1016/j.catcom.2012.11.012)

Xiufang Wang, Jun Zhang, Kehua Zhang, Wensheng Zou, Shaohua Chen, Facile fabrication of reduced graphene oxide/CuI/PANI nanocomposites with enhanced visible-light photocatalytic activity, *RSC Adv.*, 50, 01-09(2016).
[doi: 10.1039/C6RA08358G](https://doi.org/10.1039/C6RA08358G).